Nuclear Quadrupole Resonance of Nitrogen-14 in Tetracyanoethylene and 7,7′,8,8′-Tetracyanoquinodimethane

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The pure quadrupole resonance of ^{14}N in tetracyanoethylene (TCNE), $(CN)_2C{:}C(CN)_2$, and tetracyanoquinodimethane (TCNQ), $(CN)_2C : C_6H_4 : C(CN)_2$, was observed at liquid nitrogen temperature by means of a modified Pound-Watkins type spectrometer.[1] These compounds are known to be strong π-acids and form a number of unusually stable molecular complexes.[2] In attempting to discuss the nature of these chemical properties, it is worthwhile to reveal the local electronic structure of cyano groups in these compounds.

A commercial preparation of TCNE was purified by sublimation at about 80°C in a high vacuum. Purification was repeated until two closely spaced $\nu^{\rm I}$ lines were well resolved. Commercial TCNQ was sublimed twice at about 220°C in a high vacuum and used for the observation of quadrupole resonance. Resonance frequencies were determined by frequency modulation using a TR-5178 universal counter from Takeda Riken Company. Observed resonance lines were assigned to $\nu^{\rm I}$ and $\nu^{\rm II}$ by Zeeman modulation. Results are shown in Table 1.

TABLE 1. PURE QUADRUPOLE RESONANCE FREQUENCIES, $\nu^{\rm I}$ AND $\nu^{\rm II}$, QUADRUPOLE COUPLING CONSTANTS, eQq, AND ASYMMETRY PARAMETERS, η, OF ^{14}N IN TCNE AND TCNQ AT LIQUID NITROGEN TEMPERATURE

Compound	$\nu^{\rm I}$, kHz	$\nu^{\rm II}$, kHz	eQq, kHz	η,%
TCNE	3213.1±1.0 3210.2±1.0	3148.3±1.0 3090.5±1.0	4331	4.4
TCNQ	3151.6±0.1 3142.9±0.1	2888.7±0.1 2879.5±0.1	4021	13.1

Both TCNE and TCNQ show two sets of $\nu^{\rm I}$ and $\nu^{\rm II}$ lines. The appearance of multiplet lines indicates that there are two kinds of crystallographically nonequivalent nitrogen atoms in the crystals of each compound at liquid nitrogen temperature, although four nitrogen atoms are chemically equivalent in a molecule. X-Ray analysis carried out by Trueblood *et al.*[3,4] on TCNE and TCNQ has shown that both crystals are monoclinic with two and four centrosymmetric molecules, respectively, in a unit cell and that there are two crystallographically nonequivalent nitrogen sites in each crystal. The results of quadrupole resonance agree with those of X-ray analysis, provided that no phase transition takes place between liquid nitrogen and room temperatures.

The four resonance lines observed for TCNE were very broad (about 2 kHz or more in width) even after repeated sublimation. On the other hand, TCNQ showed unexpectedly sharp lines after it was sublimed only once. Since TCNE is less stable than TCNQ, field fluctuation due to decomposition products that contaminate the crystal lattice is a possible reason for the broad signals observed for TCNE. The large asymmetry parameter of TCNQ might be responsible for the appearance of sharp signals owing to quenching of dipolar broadening.[5]

For ^{14}N with its nuclear spin equal to unity, the quadrupole coupling constant and the asymmetry parameter can be calculated from observed frequencies, $\nu^{\rm I}$ and $\nu^{\rm II}$. However, for both compounds showing closely spaced doublet lines, one-to-one correspondence could not be made between $\nu^{\rm I}$ and $\nu^{\rm II}$. Therefore, the frequencies of doublet lines were averaged to calculate the quadrupole coupling constant and the asymmetry parameter as shown in Table 1.

It is noteworthy that the quadrupole coupling constant of TCNE is nearly the same as that of cyanogen[6] and is very large compared with that of nitrile derivatives.[7] The large asymmetry parameter observed for TCNQ is attributable to the nonequivalence of π-electron polarization between π-orbitals parallel and perpendicular to the plane of a molecule.

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